

to promote cleanliness. Some gasolines have over a dozen components. Diesels do not knock in the same manner as gasoline engines, but a *cetane* number is used to measure fuel quality and alkyl nitrates improve it.

HEAVY DISTILLATES. These are converted into lubricating oils,²⁵ heavy oils for a variety of fuel uses, waxes, and cracking stock. Lubricating oils of high quality can readily be made from paraffin-base oils, but most oils are mixed or naphthene base, and solvent refining is required to produce quality lubes. The Society of Automotive Engineers (SAE) has classified lube oils by means of a number system based on viscosity, change of viscosity with temperature, and severity of service. These numbers are generally used in the United States in selecting and classifying oils. A solvent extraction process for improving lube oil quality is shown in Fig. 37.7, and propane deasphalting is shown in Fig. 37.8. Additives are used extensively to improve the quality of lubes. Among those used are antioxidants, detergents, antifoams, viscosity-index improvers, extreme-pressure agents, and antiscuff agents. Viscosity, pour point, emulsibility, flash point, and resistance to sludging are important properties of lubes, generally determined by technological tests outlined and standardized by the American Society for Testing and Materials (ASTM). Synthetic lubricants,²⁶ not directly petroleum derived, are now appearing on the market and much re-refined²⁷ oil is being used.

Refined wax²⁸ is used industrially, primarily for treating paper, especially for milk cartons. Although there are many uses, synthetic waxes have sharply limited the field. Waxes are usually separated from narrow boiling point fractions, then isolated and purified by crystallization and sweating. Acid treatment or percolation through clay is used to improve the color.

Heavy distillates are used for bunker fuel for ships and in large stationary power plants, but all uses of heavy distillates are declining and the tendency is to use them as cracking stock, crack them severely in coking units (cracking units producing coke as a by-product), and convert them into products for which there is a higher demand and a better price. Sulfur content is a major determinant of the value of heavy distillates, it must be low if the product is to be readily salable.

²⁵Gillespie, Manley, and DiPerna, Making Lube Oils, *CHEMTECH* 8 (12) 750 (1978).

²⁶Synthetic Lubricants Poised for Big Growth, *Chem. Eng. News* 58 (21) 12 (1980).

²⁷Bright Prospects for Used-Oil Refiners, *Chem. Eng.* 86 (16) 28 (1979); Reynolds et al., From Oil:Oil, *CHEMTECH* 9 (10) 628 (1979).

²⁸Wax, *Chem. Week* 101 (15) 61 (1967); Bennett, *Industrial Waxes*, 2d ed., 2 vols., Chem. Publ. Co., New York, 1976.

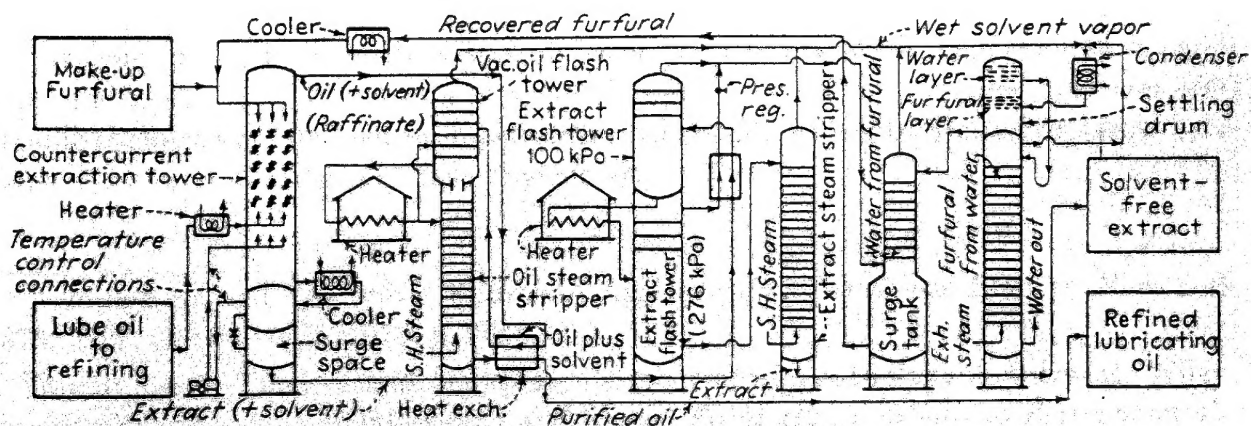


Fig. 37.7. Flowchart for lube oil refinery by furfural extraction.

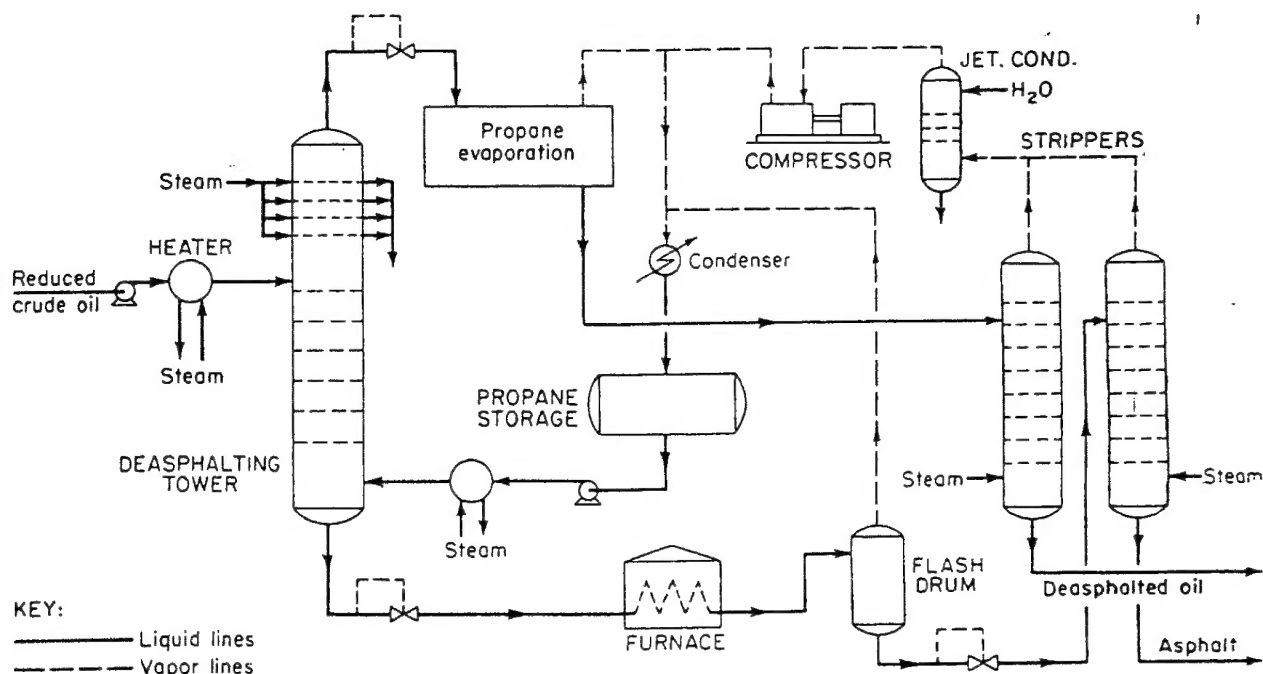


Fig. 37.8. Flowchart for lube oil deasphalting—Kellogg tower process. (M. W. Kellogg Co.)

RESIDUES. Some constituents are simply not volatile enough to be distilled, even under vacuum. These include asphalt, residual fuel oil, coke, and petrolatum. These difficultly salable materials are by-products of the refining process, and while many are extremely useful, most are difficult to dispose of and are relatively unprofitable. Petroleum coke is used commercially in making electrodes, in the manufacture of calcium carbide and ceramics, and in paints. Asphalt²⁹ finds a ready market as a road-paving material, for waterproofing structures, and in roofing material. In early times, most asphalt came from deposits in Trinidad, which are still being worked. Most is now obtained from crude residues. The properties of asphalt are markedly changed by heating it and partly oxidizing it by blowing air through it. The resulting material is known as oxidized, or blown, asphalt and is more viscous and less resilient than ordinary asphalt. It is used for impregnating roofing felt and for grouting. Hard asphalt is also used as a briquetting binder.

Greases, consisting of a divergent group of materials, fall into three classes:

1. Mixtures of mineral oil and solid lubricants
2. Metallic soap-thickened mineral oils
3. Blends of waxes, fats, resin oils, and pitches

Petroleum-derived chemicals, commonly known as petrochemicals,³⁰ are made from petroleum and natural gas. Production of some of these products is very large, and over 1000 organic chemicals are derived from petroleum (Chap. 38). Examples are carbon black, butadiene, styrene, ethylene glycol, polyethylene, etc.

²⁹Chilingarian and Yen (eds.), *Bitumens, Asphalts, and Tar Sands*, Elsevier, New York 1978; ECT, 3d ed., vol. 3, 1978, p. 284.

³⁰Rudd, Saeed, Trevino, and Stadtherr, *Petrochemical Technology Assessment*, Wiley-Interscience, New York, 1981; Hatch and Matar, *From Hydrocarbons to Petrochemicals*, Gulf, Houston, Tex., 1981; Maisel, Trends in the Petrochemical Industry, *Chem. Eng. Prog.* 76 (1) 17 (1980).

PROCESSING OR REFINING

Refining is a low-cost operation compared with most chemical processing. Crude cost was formerly far lower than now, but the Organization of Petroleum Exporting Countries (OPEC) raised the price approximately tenfold. Refining profits have been quite moderate percentages of capital costs, comparable with other phases of the chemical industry. Consider the distribution of costs of a liter of gasoline in California in 1982:

Cost of crude (Arabian)	21.4 cents
For Gasoline	
Wholesale price	25.1 cents
State and federal excise tax	2.9
Transportation and storage	1.6
State sales tax	2.1
Dealer margin	3.2
Price at retail pump	34.3
(34.3 cents/L = \$1.30 per U.S. gallon)	

Refining involves two major branches, separation processes and conversion processes. Particularly in the field of conversion, there are literally hundreds of processes in use, many of them patented. Even in a given refinery running a single crude, daily changes to accommodate changing markets and changing parameters of the conversion apparatus take place. It is the intention, therefore, of the remainder of this chapter to set forth the more important processes, show their general principles, and indicate the applications to which they may be put. No refinery on any day will operate exactly as shown, but all refineries will operate along the basic lines indicated.

Early refineries separated petroleum components into salable fractions by some type of distillation. Some chemical or heat treatment often followed to improve the quality of the crude product obtained. About 1912, the demand for gasoline began to exceed the supply, and it was presently found that the application of heat and pressure to heavier, unwanted fractions converted the large molecules into smaller ones in the boiling range of gasoline. This process, utilizing a pressure still, became known as cracking. It produced a superior gasoline because more olefins and branched chain hydrocarbons were present in the product than in straight run gasoline. This process, improved by the inclusion of active catalysts and in its methods of processing, continues to be the most important chemical process in use today. Other chemical conversions are also practiced on a very large, but lesser scale. Among them are alkylation, isomerization, hydrogenation, polymerization, reforming, and dehydrogenation.

Refineries were originally batch units with cylindrical underfired shell stills operated as "topping" units.³¹ Pumping oil continually through heaters known as pipe or tube stills and separating the constituents in continuous fractionating columns that separate many fractions between gas and asphalt is now universally practiced. Primary separation is followed by various conversion process designed to optimize yields of the more profitable and salable products. Generally this means maximum yield of gasoline. Technologically, it would be quite possible to convert the crude entirely to gasoline, but the cost would be quite prohibitive.

³¹Topping is removal of the more highly volatile constituents, leaving "reduced crude" as a residue.

ENERGY CHANGES. For many years, energy expense for refining has been the most important manipulatable cost. Conservation of heat has been the object of concentrated study. Since the sharp increase in the cost of energy, this study has been intensified. The great needs of the growing petroleum industry led to the careful study of fluid flow, heat transfer, and the properties of petroleum fractions. The industry has generated much scientific data and most of it has been made available to the scientific community. Extensive use of instruments and control systems was first made by the refining industry which now makes extensive use of direct digital control (DDC), a computer system designed to optimize variables.

SEPARATION PROCESSES. The unit operations used in petroleum refining are the simple, usual ones, but the interconnections and interactions may be complex. Most major units are commonly referred to as *stills*. A crude still consists of heat exchangers, a furnace, a fractionating tower, steam strippers, condensers, coolers, and auxiliaries. There are usually working tanks for temporary storage at the unit; frequently there are treating tanks, used for improving the color and removing objectionable components, particularly sulfur; blending and mixing tanks; receiving and storage tanks for crude feed; a vapor recovery system; spill and fire control systems; and other auxiliaries. For the refinery as a whole, a boiler house and usually an electrical generating system are added. A control room with instruments to measure, record, and control, thus keeping track of material which permits heat and material balances, forms the heart of the system. One of the major functions of the instruments is to permit accurate accounting of the materials and utilities used. Many control systems are now connected to computers which do many calculations routinely.

The following unit operations are used extensively in the separative section:

1. **Fluid flow.** Fluid flow is an operation that must not permit any unexpected failure because fire and explosion might ensue.

2. **Heat transfer.** Transfer coefficients change daily as fouling occurs. Cooling towers become less effective with time. Modern plants check the condition of the exchangers daily against computer records.

3. **Distillation.** Originally haphazard, study by the industry and universities revealed the process variables which can now be modeled and optimized with computers. When side streams are withdrawn, they contain undesirable light volatiles which are usually removed in small auxiliary towers by steam "stripping." Tower contacting material, at one time all packing or bubble caps, now consists of a variety of tower "packings" and special trays designed to reduce pressure drop while increasing vapor-liquid contact.

When the difference in volatility between components is too small for separation in a reasonably sized tower, modifications of simple distillation are used. When a solvent of low volatility is added to depress the volatility of one of the components, the separation is known as *extractive distillation*. Butenes are separated from butanes using this principle with furfural as the extractant. When a high-volatility entrainer is used, the process is called *azeotropic distillation*. Distillation to produce anhydrous alcohol from 95% solution uses benzene to free the azeotrope (Chap. 31), and high-purity toluene is separated using methyl ethyl ketone as the entrainer.

4. **Absorption.** is generally used to separate high-boilers from gases. Gas oil is used to absorb natural gasoline from wet gases. Gases which are expelled from gas storage tanks as a result of solar heating are also sent to an absorption plant for recovery. Steam stripping is generally used to recover the absorbed light hydrocarbons and restore the absorption capacity of the gas oil.

5. **Adsorption.**³² is used for recovering heavy materials from gases. Adsorbents such as activated charcoal and molecular sieves are used. Molecular sieves can select the materials recovered by molecular shape as well as molecular weight; this can be very useful. Energy can be saved by using a pressure swing absorption process wherein the material is released from the adsorbent by changing the system pressure.

6. **Filtration.** Filtration is used to remove wax precipitated from wax-containing distillates. If the cold cake is allowed to warm slowly, the low-melting oils drain (sweat out) from the cake and further purify it. Filtration in the presence of clays is known as contact filtration and has been used extensively for the decolorization of fractions. Types of filters are discussed in Perry.

7. **Crystallization.** Before filtration, waxes must be crystallized to suitably sized crystals by cooling and stirring. Waxes undesirable in lubes are removed and become the microcrystalline waxes of commerce. *p*-Xylene can be crystallized and separated from other C₈ materials by differential crystallization. For most purposes, this operation is both slow and expensive.

8. **Extraction.**³³ Extraction is removal of a component by selectively dissolving it in a liquid. This procedure is very important in preparing high-quality lube oil. Low-viscosity index materials (those whose viscosity changes rapidly with temperature), waxes, color bodies, and sulfur compounds are removed in this way (Fig. 37.7). Adequate mixing must be followed by clean and rapid separation of the two liquid layers. If a proper solvent is available, the mixture separates into two layers, one called the *extract*, which is usually solvent-rich and contains the impurities; the other called the *raffinate*, which should contain the desirable constituents and little solvent.

A process³⁴ has recently been introduced for extracting asphalt from residuum with, e.g., pentane, enabling such residuums to be used as catalytic cracking stock.

The procedure used when lubricating oil is treated with furfural is shown in Fig. 37.7, the following sequence is involved:

Continuous countercurrent extraction with furfural at 50 to 140°C, depending on the stock used.

Continuous separation of the raffinate from the extract.

Recovery of the furfural by evaporation from the raffinate.

Steam stripping to remove final traces of furfural from the raffinate.

Recovery of the furfural by atmospheric and pressure distillation of the extract.

Steam stripping to clear the extract of solvent.

Fractionation of wet, recovered furfural to give dry solvent for reuse.

Loss of solvent furfural can be cut below 0.03 percent of the solvent recirculated if the system is well run. Other solvents used for processing oil include propane, MEK, liquid sulfur dioxide, cresylic acid, dichlorethyl ether, phenol, and nitrobenzene.

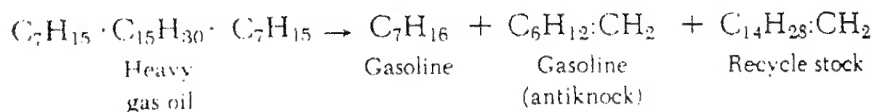
³²Breck, Advances in Adsorption, *Chem. Eng. Prog.* 73 (10) 44 (1977); Broughton, Bulk Separations via Adsorption, *Chem. Eng. Prog.* 73 (10) 49 (1977).

³³King, *Separation Processes*, McGraw-Hill, New York, 1971; Treybal, *Solvent Extraction*, 2d ed., McGraw-Hill, New York, 1963; Hanson (ed.), *Recent Advances in Liquid-Liquid Extraction*, Pergamon, Oxford, 1971.

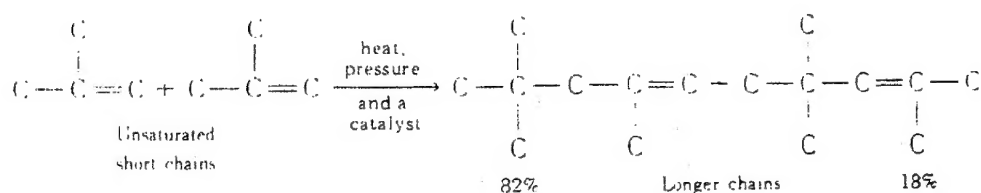
³⁴Novel Solvent Recovery Enhances Residuum Upgrading, *Chem. Eng.* 88 (24) 69 (1981).

CONVERSION PROCESSES.³⁵ About 70 percent of the U.S. crude processed is subjected to conversion processing; both carbonium ion and free radical mechanisms occur. The presence of catalysts, the temperature, and pressure determine which type predominates. The following are examples of the more important basic reactions which occur:

1. **Cracking, or pyrolysis** (Figs. 37.9 to 37.12). The breaking down of large hydrocarbon molecules into smaller molecules by heat or catalytic action. Zeolite catalysts are common; other types are also used.

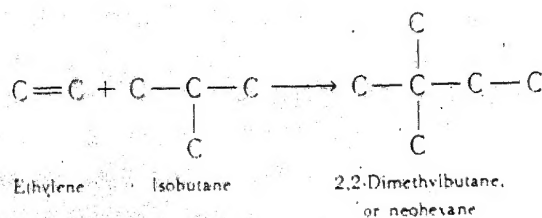
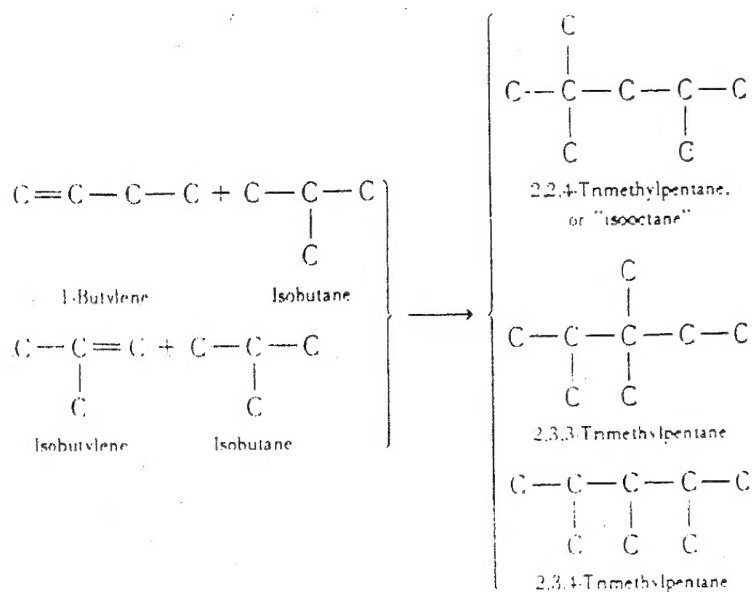


2. **Polymerization.** The linking of similar molecules; the joining together of light olefins.

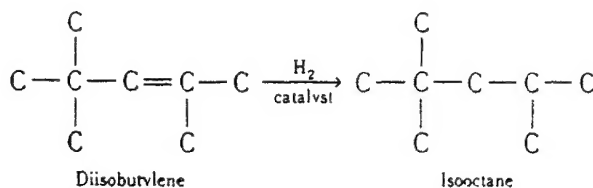


3. **Alkylation** (Fig. 37.13). The union of an olefin with an aromatic or paraffinic hydrocarbon.

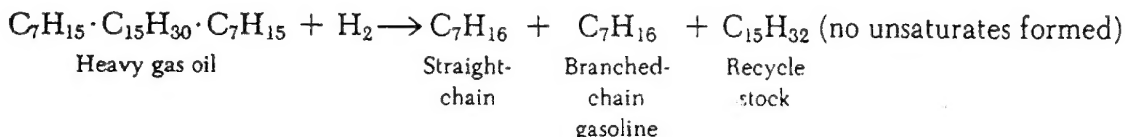
Unsaturated + isosaturated $\xrightarrow{\text{catalyst}}$ saturated branched chain. e.g., catalytic alkylation:



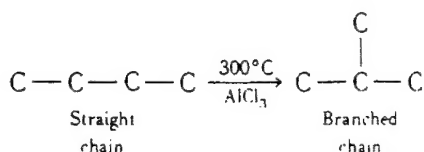
4. **Hydrogenation.** The addition of hydrogen to an olefin.



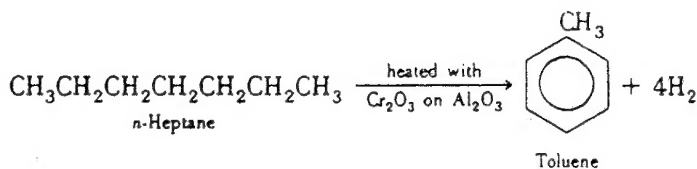
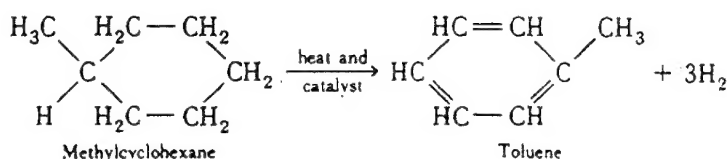
5. Hydrocracking



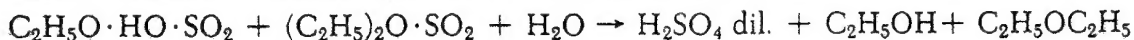
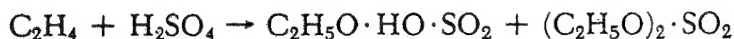
6. **Isomerization.** Alteration of the arrangement of the atoms in a molecule without changing the number of atoms.



7. **Reforming, or aromatization.** The conversion of naphthas to obtain products of higher octane number. Similar to cracking, but more volatile charge stocks are used. Catalysts usually contain rhenium, platinum, or chromium.



8. Esterification and hydration (Chap. 38).



CRACKING, OR PYROLYSIS.³⁶ When sufficient heat, preferably in the presence of a catalyst, is applied to a paraffin hydrocarbon, it breaks into two (or more) fragments, and one of them is always an olefin. The size of the fragments produced always includes all the possibilities, so the product will be a mixture. A significant amount of polymerization of the smaller molecules always occurs and some carbon is formed. The equations which follow are from Nelson³⁷ and are simplified examples, for cleavage may occur at any C—C bond.

³⁶ECT, 3d ed., vol. 17, 1982, p. 206.